Study in Electrolytic
Reduction
—
Grosvenor

A Study In

Electrolytic Reduction

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THESIS

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BY

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<div align="right">W. M. G., Jr.</div>

A STUDY IN ELECTROLYTIC REDUCTION.

PART I.

ELECTROLYSIS OF SODIUM NITRATE.

In 1879 Tommasi pointed out the reduction which occurred in electrolyzing nitrates and stated that, with sodium nitrate, the reaction yielded ammonia and ammonium nitrite. It is perhaps remarkable that so little attention has since been paid to this secondary reaction. Both theoretical[1] and technical[2] work has recently been done on the electrolytic preparation of metallic hydroxides in which nitrates served as electrolytes, but no mention was made of the extent to which they suffer reduction. The following work was undertaken to learn if sodium nitrite could not be prepared electrolytically and, if so, to determine the conditions most favorable. When the investigation was nearly completed, the writer learned that a thesis entitled "Electrolysis of Nitrates" had been submitted by Alex. Christoff, at the University of Leipzig, and a copy was immediately procured. In that paper the author has shown the effect of temperature, current density and concentration of the electrolyte upon the electro-chemical equivalents of copper and silver. He has also investigated, using insoluble electrodes in a diaphragmed cell, the effect of these conditions upon the secondary reducing action. In the latter field he confined himself to dilute solutions and operated with low current density. My own experiments were made principally with soluble anodes in concentrated solutions and with high current densities. Under these conditions, more nearly those of practical application, several perturbing factors entered, and their examination led to dis-

[1] Lorenz, Zeitschr. f. an. Ch. **12,** 436.
[2] Williams, Jour. Am. Ch. Soc., **17,** 835.

coveries of possible interest. The part of this work more or less covered by that of Christoff will be passed over with the simple statement that its results fully bear out his conclusions, *i. e.*, the nitrite formed per coulomb decreases with increased temperature, current density and dilution. This has proven to be true in concentrated as well as in dilute solutions, and with soluble as well as insoluble anodes. It was at first hoped that electrolytically liberated -NO_3ions might be largely reduced by some easily oxidized anode with the direct formation of the oxide and nitrite of the metal. The complete absence of such a reduction has been difficult to prove.

In the first attempt a six-inch side-necked U tube was used as cell in order to carefully observe the action. The cathode, a flat spiral of platinum wire, and an anode of $\frac{3}{8}''$ zinc "battery rod," heavily amalgamated, were inserted through rubber stoppers, one in each arm of the tube. This cell was half filled with a saturated sodium nitrate solution and several crystals of the salt placed at the bottom of the U. To favor oxidation of the zinc, the tube and its contents were kept at $95°$ by inclined immersion in a water bath. Application of the flame to the vertical side of the bath furthest removed from that against which the tube rested secured the formation and preservation of the hottest layers uppermost in bath and cell. Convection currents and consequent disturbance of action in the tube were thus avoided. On making the circuit (current $= 0.5$ amperes), gas was at once evolved both at anode and cathode, especially at the latter. The zinc turned black and slowly scaled off. This scale, composed almost wholly of metallic zinc, slid down the lower side of the tube into contact with the nitrate crystals and there gathered in a considerable deposit. Layer formation was soon observed below both anode and cathode. Flocculent zinc hydroxide slowly separated from the anode surface and was partially suspended, as it settled,

by the layer of separation. Even small particles of zinc were similarly held. The side-necks were fitted with delivery tubes dipping below water. Thus the cathode gas could be exploded at the surface and finally collected in sufficient quantity to burn quietly in a test tube. The anode gas was not obtainable in sufficient quantity to test. What could be obtained seemed to have no effect upon a glowing splinter. This gas was at first liberated solely upon the anode itself, but was later also slowly evolved from the piled-up zinc black. At the same time the deposit assumed a lighter color, finally becoming a grayish white, and seemed completely disintegrated to form zinc hydroxide. A sample of anode liquor then drawn and mixed with slightly acidulated potassium iodide caused an immediate liberation of iodine. After about two hours, by careful use of a pipette, the anolyte, catholyte and intermediate liquor were separately removed. All exerted strong reducing actions, the catholyte especially. This was strongly alkaline and somewhat contaminated with zinc hydroxide, while the middle solution, saturated with sodium nitrate, contained most of the precipitated matter now largely in the form of zinc hydroxide.

Cold electrolysis was then tried, using the same form of cell as before, and obtaining again rapid evolution of hydrogen at the cathode and slow disintegration of the anode. Layer formation below the cathode soon became distinctly visible, but in the other arm the layer seemed to be destroyed, perhaps by falling particles, but more probably chemical action of the two liquids. What this action could have been is hardly apparent. A few bubbles of gas appeared at the anode and zinc hydroxide formed there in small quantity. Later this gas evolution increased but bore no comparison with that at the cathode. Some slight impurities, now believed to be iron from the battery zinc, appeared as a yellow discoloration of the cathode foam. Very

little of the gradual change of the zinc black, so character-
istic of hot electrolysis, was observable at this temperature
(20° C.). The principal formation of zinc hydroxide took
place at the cathode layer, where the sodium hydroxide met
the zinc nitrate from the anode. An hour after making the
circuit, five cubic centimetres each of anolyte and catholyte
were removed with a pipette and tested with acidulated
potassium permanganate. The catholyte was strongly re-
ducing. In this case, the utmost care having been taken to
preserve the single layer formed, the anode liquor gave but
the faintest indication of nitrite. After two hours more
the anolyte and catholyte, separately removed, were tested
with permanganate; the latter showing more than thirty
times the reducing power of the former.

Several forms of cell were then tried with a view to more
perfect separation by means of the natural diaphragm, and
a number of different metals used as anodes. None of the
cells gave satisfactory results, though in all of them the
catholyte contained most nitrite. So far as its production
was concerned, different anodes behaved much alike. With
carbon, however, alike with ignited pencil graphite and with
the hardest electric light carbons, very interesting results
were obtained. The carbon anode was strongly attacked
by the acid ions, rapidly disintegrating it with the liberal
evolution of gaseous oxides. At 90° the action seemed to
completely destroy the acid, yielding carbon dioxide and
nitrogen.

Several attempts were made to prepare the nitrite in
quantity. All efforts to continuously remove the anolyte
and catholyte with replacement by water failed to give
clean separations from the sodium nitrate. To test con-
tinued action on a fixed volume of solution, a quart battery
jar was filled with saturated nitrate solution and a perforated
cylinder of zinc (active surface 484 sq. cm.) used as anode.
Within this was centrally suspended a cathode of the same

material (active surface 242 sq. cm.). Both electrodes were made soluble in order to insure the complete neutralization of nitric acid. The liquor was kept saturated with nitrate by suspending a basket of the solid salt just below its surface. A tube was so inserted, nearly to the bottom of the cell, that air forced through would bubble up along the anode surface and prevent clogging with hydroxide which greatly increases the resistance. Space was allowed at the bottom for this hydroxide to settle. The temperature of the cell remained about 25°. So little heat was generated as to suggest the consideration of energy reactions and indicate that the reduction should proceed spontaneously. Observation of the terminal difference of potential[1] supported this conclusion. The results of samples of ten cubic centimetres are here given in grams of $NaNO_2$ per c.c.

Time. Hrs.	Bath-tension. Volts.	Current. Amp.	Grams $NaNO_2$.
O	O	3.4	0.000
2:35	1.0	3.4	0.008
3:15	1.0	3.2	0.012
5:15	1.2	2.8	0.015
12:00	0.7	4.8	0.034
15:00	0.5	4.8	0.054

At about seventeen hours excessive reduction was, for the first time, detected by ammoniacal odor. The electrolysis was therefore stopped and the electrolyte tested for ammonium salts. It appeared, however, that at this concentration sodium nitrite, possibly accompanied by some hyponitrite,[2] were the only reduction products that remained in the solution. The statement of Tommasi[3] that ammonium nitrate and nitrite are formed does not seem to apply

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[1] For this quantity, "terminal difference of potential," English has no convenient equivalent of the German "Spannung" or "Bade-Spannung," and its literal translation, bath-tension, will therefore be used. The word "Erm," (Ermann) might well be adopted for this magnitude in recognition of the anticipative work of that investigator.

[2] Tanatar, Ber. **29**, 1039 (1896).

[3] Tommasi, Traité d'Electrochimie, p. 649.

to electrolysis in saturated solution with soluble anodes. The alkalinity of the cell liquor would tend to expel ammonia as formed. Ihle[1] has shown that with nitric acid there is a certain current density required at any particular concentration before the formation of ammonia is possible this limit rising rapidly with increase of concentration and at 85.37 % reaching $N.D._{.1} =$ 8.6 amperes. His results are expressed in the accompanying figure, in which the curve a b c is the locus of minima. If now the nitric acid equivalent of the electrolyte used be calculated we find, saturated at 25°, sodium nitrate solution contains 47.5 % of $NaNO_3$ as deter-
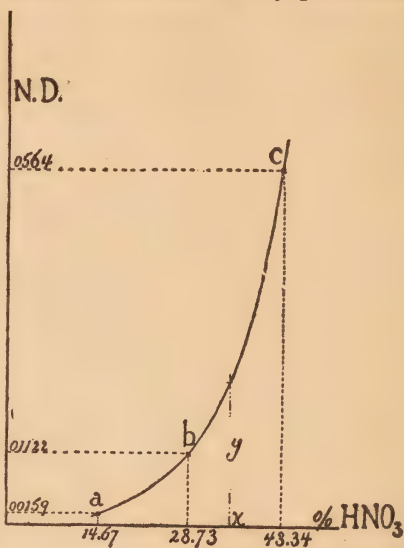

FIG. I.

mined by Mulder[2], slightly more according to Maumerre[3]. This 47.6 % corresponds to 35.2 % of nitric acid, giving the limit of normal density per square centimetre of cathode surface, $y = 0.022A$. For the cathode surface used this would demand a current of 5.3 amperes. This is well in excess of that actually employed. The margin is even wider if the degree of dissociation of nitric acid as compared with that of sodium nitrate be considered. The nearest comparable figures on molecular conductivity are for 22 % solutions[4]. Here the dissociation of nitric acid is 42.1 %

[1] Ihle, Zeitschr. f. phys. Ch. 19, 572 (1896).

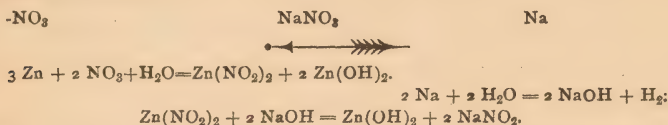[2] Mulder, Scheikundige Verhandelingen e. O., 1864, 83.

[3] Maumerre, Compt. rendus, 58, 81.
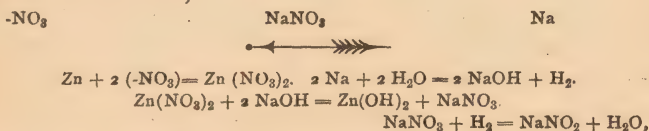
[4] Fitzpatric, B. A. Report, 1893.

against 63.3 % for sodium nitrate. Several attempts were made to find for the sodium salt a limit of current density similar to that for nitric acid, but entirely without success. The electrolyte of the above experiment was evaporated to dryness and yielded after dehydration and gentle fusion a product containing about 35 % of nitrite, contaminated slightly with iron and zinc, principally with nitrate.

It has been hoped that the reaction would proceed somewhat as follows :

$$-NO_3 \qquad\qquad NaNO_3 \qquad\qquad Na$$

$$\bullet\!\longleftarrow\ \longrightarrow\!\!\ggg$$

$$3\ Zn + 2\ NO_3 + H_2O = Zn(NO_2)_2 + 2\ Zn(OH)_2.$$
$$2\ Na + 2\ H_2O = 2\ NaOH + H_2;$$
$$Zn(NO_2)_2 + 2\ NaOH = Zn(OH)_2 + 2\ NaNO_2.$$

This reaction might be expected to proceed almost quantitatively yielding 1.28 grams of nitrite per ampere-hour. The results so far as obtained, however, appeared to indicate a cathode reduction ;

$$-NO_3 \qquad\qquad NaNO_3 \qquad\qquad Na$$

$$\bullet\!\longleftarrow\ \longrightarrow\!\!\ggg$$

$$Zn + 2\ (-NO_3) = Zn\ (NO_3)_2. \quad 2\ Na + 2\ H_2O = 2\ NaOH + H_2.$$
$$Zn(NO_3)_2 + 2\ NaOH = Zn(OH)_2 + NaNO_3.$$
$$NaNO_3 + H_2 = NaNO_2 + H_2O,$$

a reduction by nascent hydrogen which could not be expected to be quantitative and would decrease in efficiency with increasing current density. The anode reduction would, if anything, increase with concentration of the $-NO_3$ions, $i.\ e.$, with current density. Christoff advances, in support of the theory[1] that the reduction takes place by direct action of the cat-ions, the facts that nitrates of copper and silver, metals which do not decompose water at ordinary temperatures, still yield nitrites upon electrolysis.

Pursuing the suggestion of the above reactions, quantitative evidence was sought as to the part played, if any, by the zinc anode in the reduction. Short wide test tubes of slightly more than 100 c.c. capacity were used as cells, and

[1] Le Blanc, Zeitschr. f. phys. Ch. 12, 333 ; 13, 163, or "Ele o-chemistry" ('96), pp. 260 and 266.

in all cases 100 c.c. of sodium nitrate as electrolyte. The nitrite formed was estimated either by dilution of the cell content to 250 c.c., severe shaking to evenly distribute the zinc hydroxide and quickly taking a 25 c.c. sample, or by use of the entire cell content. In either case, the sample to be estimated was added to an acidulated excess of potassium permanganate and the excess titrated with ferrous ammonium sulphate. Platinum foils of areas as given (C) were used as cathodes. The area of zinc anode exposed (A) was limited by sections of rubber tubing stretched over the thin plates one-half inch wide and varying only in length exposed. The results are given in the table appended under A, the anode areas in square inches; C, cathode areas; D, the dilution in fractions of saturation at $20°$; T, the temperature, and R, the total nitrite formed expressed in grams. Q is the nitrite that should have been formed had all the cat-ions liberated been utilized in reduction. All the cells of a single experiment were coupled in series and the currents varied between 0.2 and 0.5 amperes. In Experiment V. all the anodes were of equal size and are therefore not given.

TABLE I.

Experiment I. Q = 3.82 g.

Cell No.	A.	C.	R.
1 . . . . 0.94		0.27	3.38
2 . . . . 0.64		0.27	2.48
3 . . . . 0.62		3.80	3.04
4 . . . . 0.33		0.33	2.83
5 . . . . 0.32		0.27	3.33
6 . . . . 0.32		1.50	3.30
7 . . . . 0.29		3.80	2.93

Experiment II. Q = 1.856 g.

Cell No.	A.	C.	R.
1 . . . . 1.67		0.27	1.90
2 . . . . 0.74		0.27	1.88
3 . . . . 0.44		0.27	1.85

Experiment III. $Q = 2.785$ g.

Cell No.	A.	C.	R.
1	1.26	3.8	2.65
2	1.22	3.8	2.63
3	1.29	0.29	2.05
4	1.08	0.29	2.10
5	0.39	0.29	2.30

Experiment IV. $Q = 1.803$ g.

Cell No.	D.	A.	C.	R.
1	$\frac{1}{1}$	1.31	0.85	1.53
2	$\frac{1}{2}$	1.35	0.85	1.58
3	$\frac{1}{4}$	1.32	0.85	0.88
4	$\frac{1}{15}$	1.36	0.85	1.21
5	$\frac{1}{15}$	0.60	0.29	0.64
6	$\frac{1}{15}$	0.30	0.71	0.71

Experiment V. $Q = 3.09$ g.

Cell No.	T.	C.	R.
1	10°	3.80	2.49
2	98°	3.80	2.68
3	10°	0.85	3.01
4	98°	0.85	2.10
5	10°	0.29	2.97
6	30°	0.29	2.99
7	98°	0.29	2.01

These twenty-eight results are hopelessly irregular, and a cause was sought and discovered in the anode impurities. It was found that a piece of commercial zinc, when immersed for several days in concentrated nitrate solution, caused reduction of the latter and formation of zinc hydroxide. Several lots of zinc were obtained, and all save one sample of " C. P. redistilled " gave this evidence of considerable impurity. To learn with certainty whether this action was due to local electrolysis between the zinc matrix and particles of enclosed impurity or to the action of mer-

cury with which the zinc might have been at some time amalgamated, the "activizing"[1] of the zinc, comparisons were made between the following "pairs" by immersion for a week in saturated sodium nitrate solution. The resulting reduction is given in cubic centimetres of $\frac{N}{100}$ potassium permanganate solution required for reoxidation.

Zinc "C. P. redistilled" . . . . 1.3 c.c.

Zinc   "   partially amalgamated 8.2 c.c.

Zinc   "   and platinum, with ends soldered and joint covered by rubber . 7.1 c.c.

Zinc   "   and iron similarly arranged . . . . . 4.0 c.c.

Zinc, commercial, not amalgamated . . . . 13.6 c.c.

These results seem to indicate that the effect of commercial zinc is due, at least largely, to local electrolysis. They are, however, much too small to explain the irregularities of the preceding experiments, though serving to account for the apparent paradox of many results exceeding Q. It is also to be remembered that, at the anode of a decomposition cell, the local electro-motive forces are much higher and the consequent production of nitrite much larger because the inequalities of composition are no longer submerged in neutral sodium nitrate, but are acted on by free acid or -NO_3ions which are being liberated by the primary current upon the face of the electrode. But it is apparent that, in any comparison of electrolyses using soluble anodes, the latter should consist of the purest material obtainable.

Two experiments of such comparisons are given below, the numbers under A and C being the ratios of anode and cathode areas respectively.

[1] Wislecenus, Jr. fr. pr. Ch., **54**, 18-65.

TABLE II.

Experiment VI.

Cell No.	A.	C.	T.	R.
1 1		2	11°	2.475 g.
2 1		2	92°	2.073
3 2		1	11°	2.010
4 2		1	92°	1.415
5 2		2	11°	2.106
6 2		2	56°	1.510
7 2		2	92°	2.363
8 2		3	11°	2.402
9 2		3	56°	2.320
10 2		3	92°	1.605
11 3		2	11°	2.552
12 3		2	92°	2.574

Experiment VII.

Cell No.	A.	C.	T.	R.
1 1		2	10°	1.312 g.
2 1		2	93°	broke
3 2		1	10°	1.300
4 2		1	93°	1.322
5 2		2	10°	1.333
6 2		2	53°	1.125
7 2		2	93°	1.229
8 2		3	10°	1.088
9 2		3	53°	1.404
10 2		3	93°	1.149
11 3		2	10°	1.282
12 3		2	93°	1.303

In these experiments also the results are too irregular, and in seeking an explanation, the character of cathode surface was examined and also the effect of pressure variations,

it being barely possible that irregular depths of immersion caused the difficulties.

Two cells of the same shape and size were provided with similar anodes of pure zinc and with platinum-foil cathodes of the same shape and area. The latter were immersed till the upper edges barely raised a slight meniscus. The two cathodes were cut from the same piece of foil, and trial runs of both cells in series showed them to be of very nearly equal nitrite efficiencies. One of the cathodes was now roughened with emery dust. Instead of agreeing to within 0.5 % as before, when run in series they now gave the following results:

Experiment VIII. 0.2 Amperes.

Test No.	Smooth.	Rough.	Difference.
1 . . . . . . 4.553		4.253	+6.59%
2 . . . . . . 4.417		3.969	+10.14%
3 . . . . . . 5.153		4.448	+13.68%
4 . . . . . . 4.653		4.352	+6.46%
5 . . . . . . 4.305		4.174	+3.04%
6 (2) 3.724		3.924	—5.91%
7 (3) 4.162		4.164	—0.05%
8 . . . . . . 4.833		4.472	+7.47%
9 (1) 4.431		4.360	+1.55%

Experiment IX. 0.1 Amperes.

Test No.	Smooth.	Rough.	Difference.
1 (2) 4.004		3.997	+0.17%
2 (3) 4.211		4.098	+2 68%
3 . . . . . . 4.302		4.054	+5.76%
4 (2) 4.217		4.079	+3.27%
5 (3) 4.203		4.040	+3.88%
6 (4) 4.351		4.238	+2.60%

Roughening the cathode has beyond doubt the effect, as might be expected, of increased current density on the

nascent hydrogen reduction, *i. e.*, decreasing its current efficiency. It may well be supposed that this is due to rapid localized deposition of the cat-ions exhausting, at the relatively few points of liberation, the material to be reduced and thus associating to molecular hydrogen before coming into contact with the nitrate.

Further, the results obtained hint at the possibility of another cause of irregularity in the earlier experiments. Those tests made with fresh, hitherto uncorroded zinc anodes are unmarked, while a parenthesis following the test number indicates that a corroded anode, exhibiting the crystalline structure of the metal, was employed. The numerals in the parentheses indicate the number of times it had been previously employed and, after each use, cleaned by washing, brief immersion in dilute sulphuric acid and careful rewashing. Examining these figures and the corresponding differences in efficiency, it is difficult to believe that crystalline structure of the anode surface is wholly without its influence. An influence peculiar in that it appears soon to reach a maximum with repeated use, after which to decrease.

It was suspected, from the way in which the metallic hydroxide formed about the electrodes and reached out across the intervening space, that it might influence current efficiency, possibly even short circuiting the cell. Many attempts were made either to restrain this hydroxide or to secure a heavier and more granular formation. Anodes of copper, lead, iron and mercury were tried. These were enclosed in bags of parchment and of silk and the space between the electrodes packed with glass wool, but all to no purpose. In every case, after a few minutes run, either the anode metal or its hydroxide was found clinging to the cathode. A current of 0.1 ampere, applied till 100 c.c. of electrolytic gas had been liberated in a Bunsen voltammeter placed in series with the cells, gave:

Anode of	Smooth.	Rough.	Difference.
Zinc, bagged with silk	1.685	1.639	+ 2.68%
Zinc, stuffed with glass wool .	0.761	0.856	—12.48%
Copper	1.602	1.585	+ 1.06%
Lead	0.917	0.903	+ 1.53%
Iron	0.676	0.744	—10.06%
Mercury	0.788	0.959	—21.70%

An attempt was made to study the influence of pressure upon the reduction, but the facilities for carrying the work out satisfactorily were not available. Sufficient was done, however, to indicate that considerable changes of pressure would alter the yield of nitrite, but to so slight an extent that, within the range from 0 to 2 atmospheres, the pressure effects were usually masked by other perturbations.

Quantitative study of the effects of anode and cathode density did not seem to promise much help in solving the question of anode reduction. Single-diaphragmed cells were tried and found doubly unsatisfactory. Not only did nitrite very soon appear in the anode compartment, but zinc hydroxide was rapidly precipitated in the pores and on the surface of the partition, greatly increasing the resistance and soon becoming a source of much heat. A three compartment cell was therefore built of glass and fitted with diaphragms of parchment, D (see Fig. 2). It consisted of three cylindrical chambers, perforated at S to permit of sampling, and united end to end by short sections of Gooch tubing. For convenience's sake both diaphragms and the rubber bands were firmly attached, as indicated in the figure, to the middle cylinder. This left the end compartments open for insertion of the electrodes carried by rubber stoppers closely fitting into the properly provided necks. These electrodes were of circular active surface, the anode cut from heavy sheet of pure zinc, the cathode from

platinum foil, each provided with a connecting rod soldered to its back, and the inactive surface of the electrode, the joint and the rod protected by a coat of rubber paint. The compartments were of such a size that, filled to the level of the line ll, each contained with electrodes in place 100 c.c. Samples—at first of 10 c.c. but, as nitrite content increased, 5 c.c. were sufficient—removed at the times stated were examined for nitrite as hitherto, an equal volume of saturated sodium nitrate solution being immediately added to the original charge to maintain the volume constant.

Experiment X.

Time. Hours.	A.	M.	C.
0	0.00 g.	0.00 g.	0.00 g.
1	0.00	0.00	0.10
3	0.06	0.05	0.40
5	0.12	0.07	0.62
7	0.13	0.08	0.94
9	0.15	0.20	1.21
11	0.19	0.28	1.41

Current used for Experiment X varied between 0.6 and 0.7; for XI, between 0.2 and 0.3.

Experiment XI.

Time. Hours.	$A_p.$	$A_z.$	$M_p.$	$M_z.$	$C_p.$	$C_z.$
0 . .	0.0 g.	0.0 g.	0.0 g.	0.0 g.	0.0 g.	0.0 g.
1 . .	0.0	0.00	0.00	0.00	0.031	0.046
2 . .	0.0	0.015	0.031	0.046	0.374	0.220
3 . .	0.0	0.032	0.000	0.064	0.580	0.387
5 . .	0.0	0.142	0.032	0.114	1.092	1.027
7 . .	0.0	0.196	0.094	0.229	1.599	1.702
10 . .	0.0	0.331	0.131	0.381	1.961	2.736

By this means the above results could be calculated as given in Experiment X into total grams of nitrite formed, A in the anode, M in the middle and C in the cathode

compartments. The first of the two experiments was made at a temperature of about 85°, and it is difficult to avoid the conclusion that at high temperatures some anode reduction does occur.

The second experiment was conducted with two similar cells in series, differing only in that one was provided with an anode of platinum foil as nearly like the zinc anode of the other in size, shape and position as possible. The sampling was carried out as before and the results appear under A_z, M_z and C_z for the cell provided with a zinc anode, under A_p, M_p and C_p for that with a platinum anode.

The peculiar results in M_p during the first few hours are probably due to irregular diffusion back into M of ozone
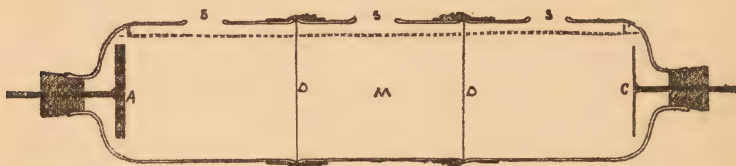
FIG. 2.

which was found in considerable quantity or of some peroxide formed in the solution. As would be expected from the ozone formation, no nitrite was found in A_p and an increasing difference is observable between M_p and M_z. The obtaining of an average sample from these compartments was a matter for some care, but by repeated filling and forcible discharge of the sampling pipette, a thorough mixing of the contents was made before the sample for analysis was drawn.

The small values for nitrite in A_z do not absolutely prove the absence of anode reduction even in cold electrolysis. But, considering the way in which they follow from the very first those of M_z, it seems strongly probable that any nitrite present in A_z came there by diffusion.

PART II.

REDUCTION OF AROMATIC NITRO-BODIES.

The interesting discussion as to the exact procedure of successive steps in reduction taken by aromatic nitro-bodies when subjected to cathode action in acid or alkaline solution, and the still open question just what the steps and their causes may possibly be, suggested the electrolytic reduction of the nitro-salicylic acids, as the products might undergo some secondary reactions or condensations throwing light upon this question. Beilstein[1] has reduced the 5-nitro-salicylic with tin and hydrochloric acid, and Gattermann[2] by cathodic hydrogen in concentrated sulphuric acid solution. Both obtained the unstable 5-amido-salicylic acid and its salts. The reduction of the 3-nitro-acid has been tried, but without result, the corresponding amido-body never having been obtained. Alkaline reduction appeared to hold out promise of better results.

Nitration of salicylic acid in acetic acid solution by addition of fuming nitric acid gave excellent yields of both the ortho- (3) and meta- (5) nitro-acids.

(3) M. P. $+1H_2O = 125°$ (5) M. P. $= 228°$
          anhydrous $= 144°$
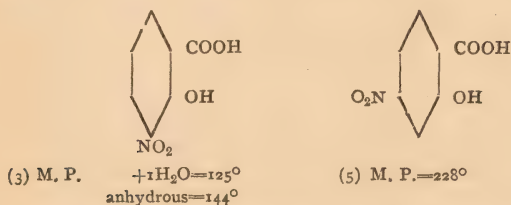
The low melting acid was first electrolyzed, using a cell of the form shown in the figure (Fig. 3). The object of this construction was to prevent free air access to the catholyte and provide for separate condensation of both

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[1] Annalen (Liebig's), **130,** 243.

[2] Berichte, **26,** 1850.
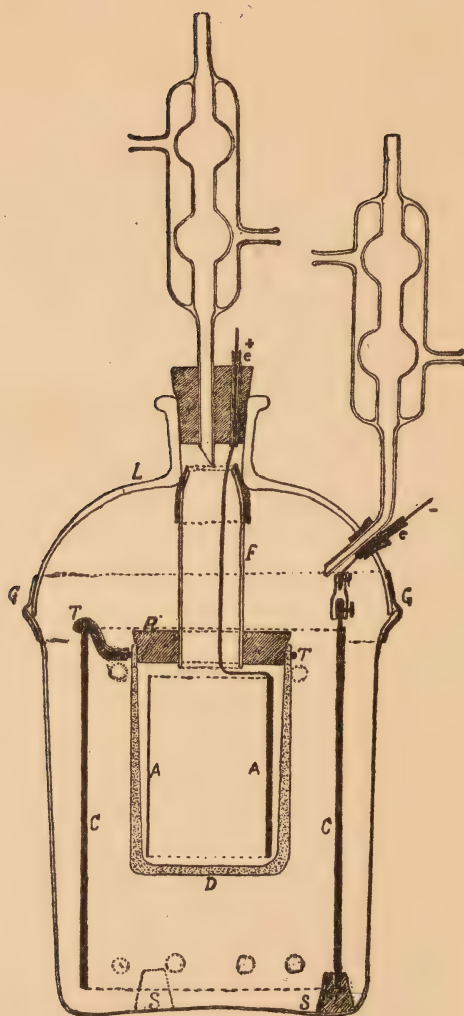
Fig. 3.

A, Anode of platinum. B, Beaker, external vessel. C, Cathode
of nickel, perforated for free catholyte circulation. D, Porous cup.
R, Rubber stopper. F, Anode flue for gas exit. T, Iron wire circlet,
with three rubber-covered arms, supporting D and F against L, the
cell cover. S, Rubber shoes supporting C. G, Wide rubber band
uniting bath and cover. e, Glass conductor-exits, fitted in operating
with rubber tubes, the latter then wired tight against the con-
ductors.

(20)

anolyte and catholyte distillates and then return to their respective compartments, making the cell available at high or low temperature. The anode liquor used was a twenty per cent. sodium hydroxide solution and the catholyte consisted of 25 g. of the acid and 45 g. of sodium hydroxide in about 1700 c.c. of water. The current applied was taken from 110 volt terminals cut down by lamp resistance to yield about 3 amperes. The bath-tension varied considerably with extent of reduction, ohmic resistance of the cell and, later, with physical polarization.

Upon making the circuit the catholyte rapidly became darker in color, soon a deep black, but after the lapse of about six hours the reverse change began, continuing until after eleven hours a light sherry brown was attained. The total duration of the experiment was fourteen hours, or until after half an hour of free hydrogen evolution. Portions of this liquor on contact with air became quite black, but no precipitate appeared even on acidification with dilute hydrochloric acid. A portion was therefore placed in a separatory funnel, acidified, and shaken out with ether. The ether immediately became dark red and, on evaporation, yielded a surprisingly small residue of a purple, crystalline, brilliantly iridescent body the slightest traces of which imparted a strong color to any solvent. On standing in glass vessels, this solution communicated to the glass a purple color quite difficult to remove. This body gave no melting point, left a voluminous residue on ignition and could be obtained only in minute quantities. Another portion was acidified, evaporated gently to dryness and extracted in a Soxhlet, yielding a small quantity of red amorphous powder apparently identical with the body before obtained, as both were sparingly soluble in water, alcohol and ether, but readily in ammonia, and this ammoniacal solution gave precipitates with ammoniacal silver and copper solutions. The silver salt was purple and somewhat flocculent. An

attempt was made to purify these salts, but without success,
as even the barium and sodium salts appeared to be un-
stable.

Another electrolysis was made and the alkaline liquor
concentrated to small volume. This was acidified out of
air contact by drawing up into a large separatory funnel
already containing a layer of ether upon one of dilute hy-
drochloric acid. After closing the stop-cock, gentle agita-
tion generated sufficient heat of neutralization to boil the
ether, and when its vapors had expelled the air from the
funnel globe, the stopper was tightly inserted and the mix-
ing slowly completed under cold water. This ether extract,
removed and evaporated in vacuo, yielded but a trace of the
same beautiful body resembling a dye base. This still left
a large residue on ignition. Further examination of the
liquors failed to yield anything but gummy decomposition
or polymerization products which were not purified or
identified.

Hoping for better success with the high-melting acid,
varying quantities were electrolyzed in the same manner as
was the low-melting acid. The quantities taken were : A,
25 g.; B, 15 g.; C, 20 g.; D, 20 g. The behavior of the cath-
olyte during reduction and the time required were about
the same as before described.

Of the liquor yielded by A, part was allowed free air
contact before acidification, part acidified under ether as
above described, both yielding apparently the same result.
In spite of the fact that the sample which was allowed air
contact rapidly became dark, the precipitate which formed
in small volume on acidification was apparently stable in
air and identical in both samples, although that acidified
under ether was filtered and dried in an atmosphere of
hydrogen. B was tried partly with a view to learning the
effect of greater acid-dilution of the catholyte, partly to use
different solvents in an attempt to shake out the product of

acidification as formed, but, briefly, to no purpose. C was tried in an attempt to crystallize the substance by very securely stoppering the separatory funnel just as the ether was completely expelled, shaking vigorously and then allowing to cool very slowly. This promised good results, for in addition to the red precipitate which had defied all efforts at purification, a few clearly defined brown crystals formed on the walls of the vessel. By great pains these were removed and dried in hydrogen. They then appeared to be stable in air, burned without trace of residue and melted sharply at 242° with slight carbonization. They proved to be almost insoluble in cold water, very slightly in hot. They dissolved readily in ammonia to a red liquor, from which solution on acidification the familiar red precipitate was obtained. The body appears to be readily oxidized in alkaline solution, for boiled with dilute hydrochloric acid it does not impart the red coloration to the liquor observed after acidification of an ammoniacal solution as well as in the filtrate from the red precipitate. This body was not analyzed because it appeared in so small a quantity (0.1 g.) and repeated efforts to reproduce it under similar conditions failed completely. The red precipitate was treated with alcohol, ether, chloroform and benzene in attempts to purify it by crystallization or fractional extraction, and was many times dissolved and reprecipitated, but no apparently pure product could be obtained.

m-Azo-benzoic Acid.

Failing then to obtain satisfactory results from the reduction of these nitro-salicylic acids, simpler nitro-benzene substitution products of related character were taken up in the hope that they would throw light upon the tendency of the separate groups toward condensation of the nitro-nuclei when subjected to electrolytic reduction in alkaline solution. The first tried was the carboxyl substitution, m-nitro-

benzoic acid being selected. It is already known that nitro-benzene upon electrolytic reduction in alkaline solution yields oxazo-, azo- and hydrazo-benzene at various stages of the reduction. Azo-benzoic acids might, therefore, not unreasonably be expected as reduction products of the corresponding meta- and para-nitro-acids. Whether the presence of the carboxyl group in the ortho position would lead to condensation cannot, a priori, be predicted but it seems hardly likely. The meta acid is the one bearing most directly on the problem under consideration and the only one so far examined. In this case anticipation was fully realized.

Fifty grams of m-nitro-benzoic acid were dissolved in the same catholyte previously used and electrolyzed in the same cell for fourteen hours, using a current of three amperes (N.D.$_{100}=$ 0.7 amperes). The catholyte passed through much the same changes as with other nitro-bodies. In this case, no condensation being anticipated, free air access was allowed the reduced liquor and consequent darkening rapidly took place without production of any precipitate. On acidification, a quantity of slate-colored, slimy precipitate appeared. After allowing to stand for some time to complete the precipitation, this was filtered off. The resulting slime was dried on a porous tile, pulverized, mixed with bone black and extracted with alcohol. A golden yellow extract resulted which, on evaporation, deposited about 20 g. of crude m-azo-benzoic acid, identified by its salts, physical properties and finally, by a carefully purified sample, with Strecker's[1] light, yellow, amorphous powder, $C_{14}H_{10}N_2O_4.\frac{1}{2}H_2O$, and giving by analysis

|	Theoretical.	Strecker.	Found.		
C . .	60.22	60.26	59.77	59.76	59.88
H . . .	3.94	3.90	3.88	3.96	4.14
N . . .	10.04	10.10	10.99	10.91	

[1]Annalen (Liebig's), 129, 134.

Strecker first prepared the body by the usual method of alkaline reduction and found the half-molecule of water was not removed by heating to 170°. The sample above analyzed was dried at 125° after recrystallization from alcohol and then given a long period of vacuum dessication over sulphuric acid.

o-Amido-phenol.

The next step in the investigation of substituted groups was naturally the reduction of ortho-nitro-phenol. To this end :

(*A*) 25 grams of the purified substance were dissolved in the same catholyte and electrolyzed in the same cell, $N.D._{100}=0.6$ amperes, for twenty hours at a temperature of 30° to 35°. The time was somewhat in excess of that required for complete reduction. The liquor passed through the same general color changes as had the others, ultimately becoming a pale claret-color. Being in this case suspicious of the effect of oxidation, portions were removed as before described without air access and using only enough acid to generate, with *part* of the excess caustic, the heat required to volatilize the ether (or ligroin), only small portions of which were used where other solvents were to be tested. Shaken thus with various solvents, ether, chloroform, benzene and ligroin, the still alkaline liquor apparently yielded nothing to the solvents. On air access it immediately became a deep red color, almost black. Of these same solvents used after acidification benzene and chloroform showed the best solvent power, especially the latter. The chloroform solution was at first a clear golden yellow, without peculiar optical properties. Soon, however, it became slightly reddish in tinge and exhibited the most striking green fluorescence—due as indicated by later tests to the effect of slight access of oxygen. This, in connection with the recent work of R. Meyer[1], seemed to indicate

[1] Meyer, Zeit. f. phys. Ch. **24,** 468.
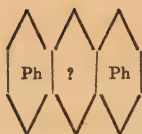
a condensation of this general form, and the groups enter-
ing therein, OH and NH_2, pointed to phenazine or phena-
zoxine condensations as most probable, a fact of much
interest in view of the behavior of the o-nitro-salicylic acid.
The entire cell content was therefore acidified, allowed free
air access and shaken out with chloroform. Air was blown
through this extract, giving it a darker red color and even
richer green fluorescence. On evaporation it yielded, con-
sidering the strong coloration of the solution, a surpris-
ingly small quantity of solid residue (perhaps 0.05 grams
from four litres of the extract). This residue consisted of
a granular red powder, quite soluble in alcohol and ether
and quite impure, since it not only left a large residue on
ignition but on several recrystallizations from alcohol
ceased to leave this residue, assumed a brick-red color and
gave successively rising melting points of 230°, 250° and
275°, at the latter point melting with simultaneous decom-
position and a faint yellow sublimate. This purified product
dissolved readily in concentrated sulphuric acid with deep
red coloration. This on dilution became yellow and neither
solution showed fluorescence. A small portion dissolved
in chloroform gave a straw-yellow liquid, permanent on air
exposure, and again showing the rich green fluorescence.
It was further noticed that the mother liquor from which,
by repeated shaking with chloroform, nearly all the red
body had been removed, if then allowed to stand for a day
or two was again and repeatedly in position to yield small
portions of the same body—enough to strongly color several
hundred cubic centimetres of chloroform. An attempt to
increase this yield by blowing air through the mother liquor

proved unavailing and it was therefore set aside and attention turned to increasing the yield of this product by altered conditions of electrolysis.

(B) Twenty-five grams of o-nitro phenol were dissolved in the catholyte and reduced at $15°$ by a current of N.D $_{100}$=0.3 amperes. Working thus the complete reduction required about twenty-six hours. In this case ligroin was tried as solvent for shaking out the reduction product after acidifying—it having been noticed that ether showed a stronger preference for the dark colored impurities which chloroform also brought with the substance desired. Acidification and first shaking were easily accomplished without air access and the resulting ligroin solution poured continuously into a shallow dish, the solvent being blown off by a rapid current of dry cold air. Thus a rapid evaporation was obtained at a temperature of $-10°$ to $-15°$. The residue was a pale yellow mass of woolly crystals, exceedingly small in quantity and fairly stable when once dried. The quantity was about sufficient to obtain a melting point. This was done in a long, very thin-walled tube and found to be fairly sharp at $34°$, without apparent decomposition, to a clear yellow oil. On further heating this oil distilled rapidly at $210°$ to $215°$ without ebullition and recondensed just above the surface of the olive oil bath as straw-yellow crystals which thereafter gave a sharp and constant melting point at $46°$. An attempt to shake out a further portion of this body yielded only a mixture of it and the previously obtained red body, and unless evaporation was very rapid, the red body only was obtained. As thus formed, it was apparently identical with that before obtained, melting quite sharply at $265°$.

(C) A third electrolysis was carried out under similar conditions except as to temperature, this time $95°$, and N.D.$_{100}$=1.2 amperes continued for about fifteen hours. This passed through the same intermediate changes, but the

final color was a pale bluish gray. The catholyte was allowed to cool before the current was interrupted and then taken up under dilute hydrochloric acid on the surface of which a few cubic centimetres of ligroin had been placed. The liquor itself was followed by quite a large volume (300 c.c.) of chloroform. *Complete* exclusion of oxygen was obtained, as the dilute hydrochloric acid had been previously boiled under reduced pressure, cooled in its own vapor and this replaced by hydrogen when the liquid was drawn up into the separatory funnel under ligroin. The cell liquor thus carefully acidified stood for days, with repeated shaking, without yielding to the chloroform an observable quantity of the greenly fluorescent matter. In fact the liquor itself retained its dull gray color. The chloroform merely took on a faint yellow tint. This answered in the affirmative, as did other subsequent tests, the question whether oxygen was necessary to the condensation which produced fluorescence. On opening the vessel to air access, the formation of the red body was seemingly somewhat slower (lack of oxygen already in solution) but the yield slightly larger than formerly. Still it was so small as to offer no encouragement to obtain the body in quantity requisite for purification and analysis. Again the successive crops were obtained. This phenomenon, in connection with the very small yield, pointed to the presence in the reaction liquor of some parent substance soluble both in acid and alkali, apparently condensing to form the pale yellow [46°] crystals so readily oxidized to the red [265°] granular body giving the green fluorescence. The fact that this parent body remained still in solution suggested its being an amido-phenol.

The mother liquor was therefore treated with an excess of sodium acetate, the resulting mixture filtered and the filtrate shaken out with ether. On the filter was obtained a relatively clean mass of leafy crystals and evaporation of

the ether yielded a second quantity, much less pure. A por-
tion of this product recrystallized from ether, boiled with
bone black, and again crystallized from the ethereal solution
under reduced pressure, yielded a gram of white, pearly,
crystal leaflets melting at 154° to 156°. This base or its
hydrochloride gave a brilliant red color with nitric acid,
and dissolved without coloration or apparent decomposi-
tion in concentrated sulphuric. The hydrochloride yielded
with ferric chloride a deep red-brown coloration in dilute,
and a black precipitate in concentrated solution. An am-
moniacal solution of the body, boiled with ammoniacal
silver nitrate, reduced the latter. In general the body de-
ported itself like either p- amido-resorcin or o- amido-
phenol, the reactions not sufficing to indicate which.
Analysis showed

	Found			Theoretical for the	
	I.	II.	III.	Resorcin.	Phenol.
C.	57.35%	57.72%	57.27%	57.57	66.02
H.	7.48%	5.39%	6.66%	5.61	6.44

Suspicions were entertained as to the correctness of the
conclusion thus indicated, since the acetate of this base
yields C= 56.78%, H= 6.52%. The body was therefore
boiled with a considerable volume of water to which bone
black had been added. In water it proved quite soluble
and the filtered aqueous solution, evaporated in a vacuum
dessicator, yielded similar crystals to those analyzed but
now melting sharply at 172°. A sample recrystallized
from ether was dried as rapidly as possible between filter
paper (the base being unstable in moist state) and the purest
parts, i. e., least colored, reserved for the last analysis, III.
Combustion now gave:

Theoretical for o-am.-phenol.	Found		
	I.	II.	III.
C. . . . 66.02	65.49	66.76	66.14
H. . . . 6.44	7.26	6.91	6.80

fully identifying the reduction product as ortho-amido-phenol [171° — 173°].*

This result is of interest in view of the facts that, as a rule, alkaline reductions yield azo-bodies and that, when amido-bodies are formed by acid reduction, an additional hydroxyl group enters the para position. This was assumed and finally proven by Gatterman[1] to take place by first formation of the hydroxylamine bodies and then rearrangement of the molecule by transposition of the OH group with the H of the para position, that investigator having caught up the intermediate product as its condensation with benzaldehyde added to the catholyte before electrolysis. The results above described show this to be but one of the ways by which electrolysis converts the nitro- into amido-bodies.

Viewing the red body in the light of this knowledge and of the facts, first, that it remained soluble in alkaline solution; second, that it was insoluble in dilute hydrochloric acid, appearing along with probably higher condensations in the dirty sediment of the acid liquor; third, as a fluorescent product obtained probably by condensation and oxidation of o-amido-phenol, it is at least a plausible assumption that the body is an oxy-phenazin produced by loss of one water molecule and four hydrogen atoms from two molecules of the parent substance according to the structural figuring
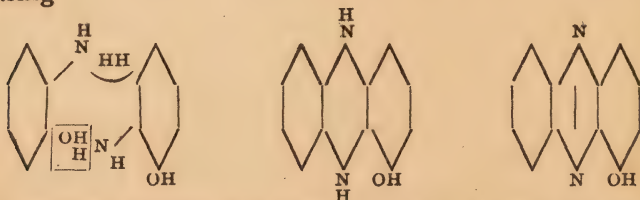
1 Gatterman, Berichte, 29, 3040.

Unfortunately no record of this body has yet been observed and several attempts to synthesize it from the phenol have as yet proven fruitless. Ortho-amido-phenol was acted on by anhydrous zinc chloride, and treated with concentrated sulphuric acid. Oxidizing agents were added to the resulting solutions and other attempts made to dehydrate or to dehydrate and simultaneously oxidize, hoping to reproduce the condensation and obtain the red body in sufficient quantity for analysis. So far all attempts have failed.

Nor does the production of the ortho-amido- from the ortho-nitro-phenol cast much light on the behavior of the salicylic acids, except to indicate the disturbing effect of the adjacent hydroxyl group upon the normal procedure of alkaline reduction from nitro-to azo-bodies. Even this does not explain the failure in the case of the high-melting acid to obtain the corresponding α β-dioxy-dicarboxylic azo- body.

ORA